Hetero π Systems, 24[◇]

Silylenes of the Elemental Composition C_4H_2Si: Generation and Matrix-Spectroscopic Identification

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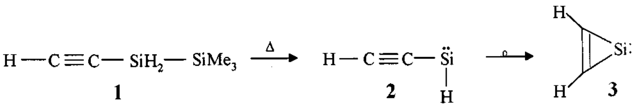
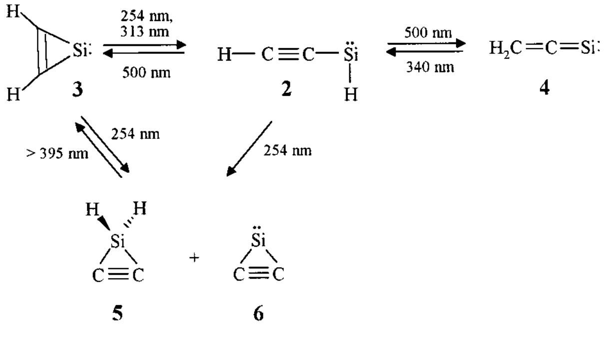
Flash pyrolysis of 1,1-diethynyl-2,2,2-trimethyldisilane (**16**) and triethynylsilane (**18**) led to the formation of two silylenes of the elemental composition C_4H_2Si, namely diethynylsilylene (**10**) and ethynylsilacyclopropenylidene (**7**), which were isolated in an argon matrix at 10 K. Both compounds could be photoconverted into another isomer, butadiynylsilylene (**9**). The identification of these reactive intermediates is based on the comparison between the experimental and calculated IR spectra for the parent compounds as well as for their dideuterated and fully ^{13}C-labeled isotopomers.

About ten years after our first matrix isolation studies of C_3H_2 isomers, namely cyclopropenylidene[1], propynylidene[2], and propadienylidene[3], we succeeded in our search for analogous C_2H_2Si isomers[4]. Pulsed flash pyrolysis of 1-ethynyl-2,2,2-trimethyldisilane (**1**) yielded silacyclopropenylidene (**3**) as a rearrangement product of initially formed ethynylsilylene (**2**).



Upon irradiation of matrix-isolated silacyclopropenylidene (**3**) its isomers ethynylsilylene (**2**), vinylidenesilylene (**4**), and – as the most attractive member of this series – silacyclopropyne (**5**)[5], were formed. Furthermore, a reversible dehydrogenation process led to the formation of already known[6] silacyclopropynylidene (**6**).



During the course of our studies of silicon π systems we found, that silylenes bearing hydrogen at the subvalent silicon atom are too unstable to be detected under *high-vacuum* flash pyrolysis conditions. This is even true if *pulsed* flash pyrolyses are applied. Therefore, in continuation of our earlier work, we were interested in generating and investigating substituted silacyclopropenylidenes and their isomers. We begin with the report about our investigations in the series C_4H_2Si.

Calculations

As there were no experimental or theoretical data concerning C_4H_2Si isomers available in the literature, we carried out density functional calculations on five species **7**–**11** of this composition, assuming, that all of them possess a singlet ground state. In addition to the energies and geometries the vibrational spectra were calculated, which are essential for the interpretation of the experimental matrix spectra.

The results of our BLYP/6-31 G*[7] calculations are summarized in Scheme 1. As expected on the basis of our earlier results with the C_2H_2Si hypersurface[5], ethynylsilacyclopropenylidene (**7**) is the most stable isomer of the selected species **7**–**11**. Surprisingly stable is cumulene **8**, especially if compared with the structurally related cumulene **11,** which is 13.6 kcal/mol higher in energy. Butadiynylsilylene (**9**) and diethynylsilylene (**10**) are nearly isoenergetic lying 12.2 and 13.3 kcal/mol above **7**.

Thermal Generation of the C_4H_2Si Silylenes

Our standard method for the thermal generation of silylenes consists in the α-elimination of trimethylsilane from

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[◇] Part 23: G. Maier, H. P. Reisenauer, A. Meudt, H. Egenolf, *Chem. Ber.* **1997**, *130*, 1043–1046.

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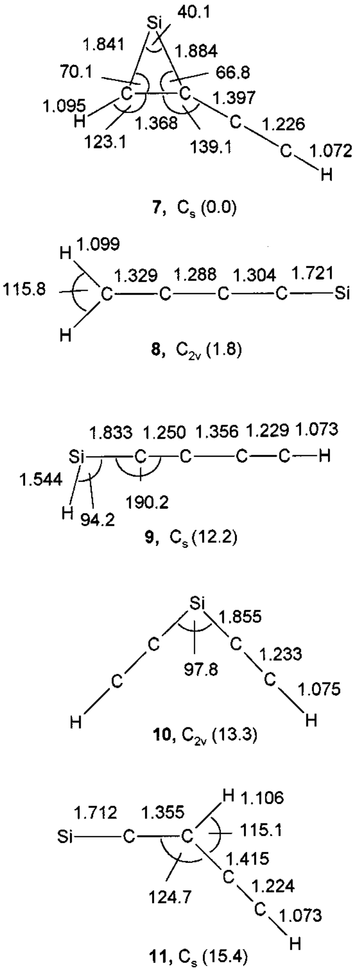
Scheme 1. Calculated (BLYP/6-31G*) relative energies (in parentheses; kcal/mol; corrected by zero-point vibrational energies) and geometries of selected C_4H_2Si isomers



suitable precursors[4][5]. In the present case, pyrolysis of 1,1-diethynyl-2,2,2-trimethyldisilane (**16**) would be the method of choice for the preparation of the C_4H_2Si isomer **10**.

In our former pyrolysis experiments with 1-ethynyl-2,2,2-trimethyldisilane acetylene was formed as a by-product[4]. Therefore, another possible pathway to **10** would be the thermal extrusion of acetylene from triethynylsilane (**18**). This compound would have the advantage to be easier accessible than **16** and the elimination product acetylene would have in contrast to trimethylsilane a very simple IR spectrum. As a consequence, a wide IR range should remain free for the observation of relevant absorptions.

$$\underset{\mathbf{12}}{Me_3Si{-}SiPh_3} \xrightarrow[< 5\ min]{HBr} \underset{\mathbf{13}}{Me_3Si{-}SiPh_2Br} \xrightarrow{LAH} \underset{\mathbf{14}}{Me_3Si{-}SiHPh_2}$$

$$\xrightarrow{2\ TfOH} \underset{\mathbf{15}}{Me_3Si{-}SiH(OTf)_2} \xrightarrow{2\ HC{\equiv}CMgCl} \underset{\mathbf{16}}{Me_3Si{-}SiH(C{\equiv}CH)_2}$$

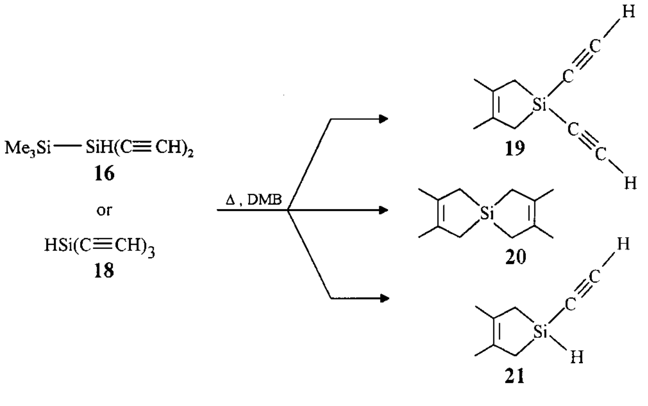
Key compound in the synthesis of 1,1-diethynyl-2,2,2-trimethyldisilane (**16**) is the previously unknown 1,1,1-trimethyl-2,2-diphenyldisilane (**14**), which should be accessible from disilane **12**. Stirring of trimethyltriphenyldisilane **12**[8] for some hours with a large excess of liquid HBr at −72°C results in the substitution of two phenyl substituents yielding 2,2-dibromo-1,1,1-trimethyl-2-phenyldisilane. Since the rate of multiple dephenylation of oligoarylsilanes goes down with increasing number of electronegative substituents at the central silicon atoms, shortening of the reaction time and using small amounts of HBr should result in the formation of monobromide **13**. This was indeed the case. Bromodisilane **13** was reduced to diphenyldisilane **14** using $LiAlH_4$ in diethylether. Successive reaction of 1,1,1-trimethyl-2,2-diphenyldisilane (**14**) with two equivalents of trifluoromethanesulfonic acid and two equivalents of ethynylmagnesiumchloride yielded the desired precursor **16,** which was isolated by preparative gas chromatography.

$$\underset{\mathbf{17}}{HSiCl_3} \xrightarrow{NaC{\equiv}CH} \underset{\mathbf{18}}{HSi(C{\equiv}CH)_3}$$

The already described[9] triethynylsilane (**18**) was synthesized by reaction of trichlorosilane (**17**) with an excess of sodium acetylide.

Trapping Experiments with 2,3-Dimethylbutadiene

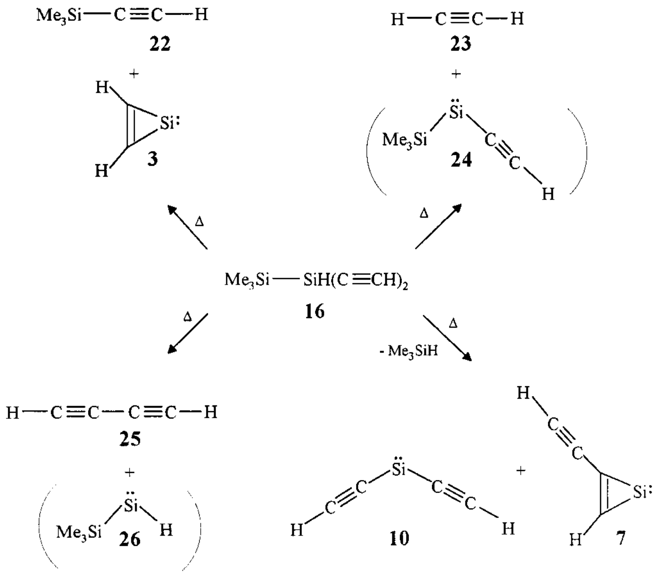
In order to test the suitability of 1,1-diethynyl-2,2,2-trimethyldisilane (**16**) and triethynylsilane (**18**) as precursors for C_4H_2Si isomers, we carried out trapping experiments with the silylenophilic 2,3-dimethyl-1,3-butadiene (DMB). Copyrolysis of disilane **16** and dimethylbutadiene led to three products. The formation of silacyclopentene **19** demonstrates the feasibility of compound **16** as a precursor for diethynylsilylene. No adducts originating from other C_4H_2Si isomers were found. Silacyclopentene **21** results from 1,1-diethynyl-2,2,2-trimethyldisilane (**16**) by α-elimination of trimethylsilylacetylene via ethynylsilylene[4][5]. The extrusion of acetylene from **21** or of butadiyne from **19** followed by reaction with one equivalent of 2,3-dimethylbutadiene explains the formation of relatively large amounts of spirosilane **20**.



Copyrolysis of triethynylsilane (**18**) and dimethylbutadiene under comparable conditions also led to the products described above, but in lower yields. It is easier to extrude trimethylsilane from **16** than acetylene from **18**. Nevertheless, these results demonstrate the principal feasibility of acetylene elimination from ethynylmonosilanes for the generation of silylenes.

Flash Pyrolysis of 1,1-Diethynyl-2,2,2-trimethyldisilane (16) and Triethynylsilane (18) in Combination with Matrix Isolation

Gaseous mixtures of diethynyldisilane **16** and argon (1:1000) were subjected to a *pulsed* flash pyrolysis (ca. 1200 °C) followed by the direct condensation of the reaction products onto a spectroscopic window at 10 K. From the analysis of the matrix IR spectra four different fragmentation pathways can be derived.



First, α-elimination of (trimethylsilyl)acetylene (**22**), which was identified by the matrix IR spectrum of an authentic sample, led to silacyclopropenylidene (**3**)[4][5]. Second, large amounts of acetylene (**23**) were formed. We found no indication for the expected co-fragment ethynyl(trimethylsilyl)silylene (**24**) or its rearrangement product (trimethylsilyl)silacyclopropenylidene in the matrix IR or UV spectra. Third, α-elimination of butadiyne (**25**) should give (trimethylsilyl)silylene (**26**). Although butadiyne was formed in considerable amounts, (trimethylsilyl)silylene (**26**) could not be found, in accordance with the above-mentioned difficulty to detect H-substituted silylenes in thermal fragmentations. Fourth, large amounts of trimethylsilane proved that the most interesting fragmentation pathway was mostly followed.

After identification of all IR absorptions of the above-mentioned pyrolysis products (**3**, **22**, **23**, **25**, trimethylsilane) many bands remained unassigned. By comparison with the results of BLYP/6-31G* calculations of the C_4H_2Si isomers **7−11**, we could show that most of these absorptions belong to diethynylsilylene (**10**) and − most likely − to its rearrangement product ethynylsilacyclopropenylidene (**7**). In case of **10** the identification follows from the good agreement between the experimental and calculated IR spectrum (Table 1, Figure 1). For **7** the structural elucidation is not possible beyond any doubt, since only relatively weak and "uncharacteristic" bands can be expected. A reasonable correlation between the observed (most prominent bands at 557.0 and 581.7 cm^{-1}) and calculated spectra can be achieved. But the main proof for **7** is its genetic connection with the two other isomers **10** and **9** (see below).

Table 1. IR spectral data (BLYP/6-31G*) of diethynylsilylene (**10**): Experimental (Ar matrix, 10 K) and corresponding calculated and corrected wavenumbers (cm^{-1}). Intensities (vs = very strong, s = strong, m = middle, w = weak, vw = very weak) in parentheses

mode		$\tilde{\nu}_{calc.}$	$\tilde{\nu}_{corr.}$[a]	$\tilde{\nu}_{obs.}$[e]
a_1 CH str		3388.6 (14)	3312.9	3312.9/3296.7 (s)
	D_2	2611.5 (1)	2552.9	2578.4/2567.2 (w)
	$^{13}C_4$	3371.5 (15)	3295.9	3296.0/3280.0 (m)
b_2 CH str		3388.4 (36)	3296.7	3312.9/3296.7 (s)
	D_2	2610.3 (3)	2539.7	2578.4/2567.2 (w)
	$^{13}C_4$	3371.3 (39)	3280.1	3296.0/3280.0 (m)
a_1 CC str		2019.9 (23)	2012.5	2012.5/2004.3 (w)
	D_2	1896.7 (28)	1889.8	1894.2/1885.8 (w)
	$^{13}C_4$	1946.9 (21)	1933.2	1940.3/1932.6 (w)
b_2 CC str		2013.0 (85)	2007.3	2007.3/1999.5 (s)
	D_2	1890.5 (100)[b]	1885.3	1888.9/1861.1 (vs)
	$^{13}C_4$	1940.3 (79)	1935.0	1935.6/1928.0 (vs)
b_1 CH def		685.2 (39)	630.0	630.0/618.9 (vs)
	D_2	538.9 (18)	495.5	–
	$^{13}C_4$	679.1 (39)	624.4	625.4/623.8 (vs)
b_2 CH def		603.3 (100)[c]	621.6	621.6/618.9 (m)
	D_2	595.6 (91)	613.6	612.6 (vs)
	$^{13}C_4$	590.9 (100) [d]	608.7	609.1/606.2 (m)
a_1 SiC str		601.3 (94)	605.9	605.9/602.4 (w)
	D_2	591.8 (65)	596.4	597.9 (s)
	$^{13}C_4$	592.0 (99)	596.6	593.7/590.3 (w)

[a] $\tilde{\nu}_{corr.} = \tilde{\nu}_{obs.}(C_4H_2Si) / \tilde{\nu}_{calc.}(C_4H_2Si) \cdot \tilde{\nu}_{calc.}(isotopomer)$. − [b] Abs. int. 123.6 km/mol. − [c] Abs. int. 121.1 km/mol. − [d] Abs. int. 121.0 km/mol. − [e] Split by matrix effects.

High-vacuum flash pyrolysis of diethynyldisilane **16** led to the same results, but the reactive intermediates **7** and **10** were found in lower yields. This is noteworthy because with 1-ethynyl-2,2,2-trimethyldisilane (**1**) this technique produced not even traces of ethynylsilylene (**2**) or silacyclopropenylidene (**3**)[4].

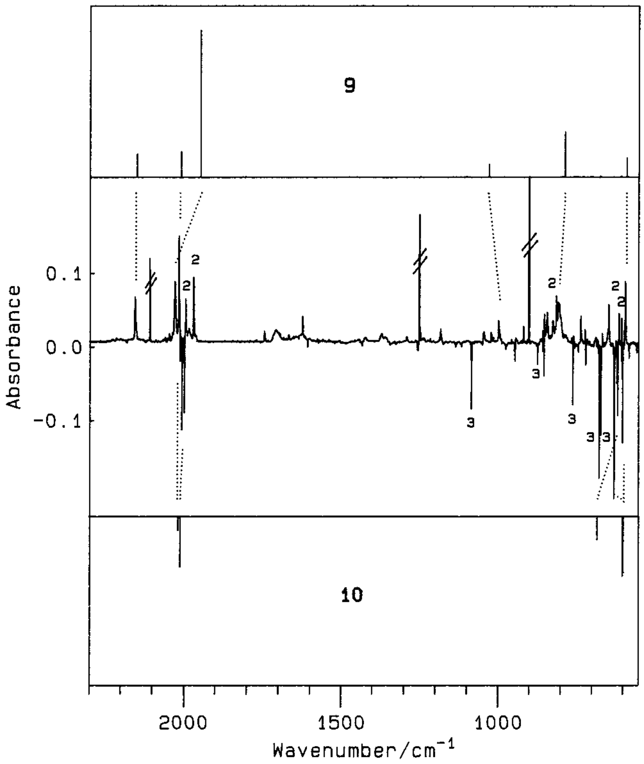
Moderate amounts of C_4H_2Si isomers **7** and **10** were also accessible by *pulsed* flash pyrolysis of triethynylsilane (**18**).

Photochemistry of the C_4H_2Si Silylenes

By irradiation of the matrix-isolated C_4H_2Si isomers **7** and **10** with light of wavelength 254 nm, the IR absorptions of both compounds diminished, and a new C_4H_2Si species was formed. Of especially high diagnostic value were its absorptions at 3328 (ν_{CH}), 2156 (ν_{CC}), 2029 (ν_{CC}) and 2016 cm^{-1} (ν_{SiH}). The good coincidence of these and all other experimentally observable vibrations with the calculated IR spectrum of butadiynylsilylene (**9**) was obvious (Table 2, Figure 1).

By a subsequent irradiation with visible light (λ >395 nm) silacyclopropenylidene **7** can be reformed from **9**. On the other hand light of the wavelength 366 nm transforms **7** back to **9**, whereas with λ = 313 nm an isomerization of **9** to **10** is initiated. Difference spectra at various stages of

Figure 1. Comparison of experimental (Ar matrix, 10 K) and theoretical (BLYP/6-31G*) infrared spectra of diethynylsilylene (**10**) and butadiynylsilylene (**9**). Bars at top: Calculated IR spectrum of **9**. Centre: Difference spectrum of the photoreaction (254 nm) **10** → **9**. Bars at bottom: Calculated IR spectrum of **10**. IR bands due to trimethylsilane are crossed. Parallel to the interconversion **10** → **9** byproduct **3** is isomerized to **2**.



the photochemical interconversions of **10**, **9**, and **7** supported the structural identifications discussed above.

C_4D_2Si and $^{13}C_4H_2Si$ Silylenes

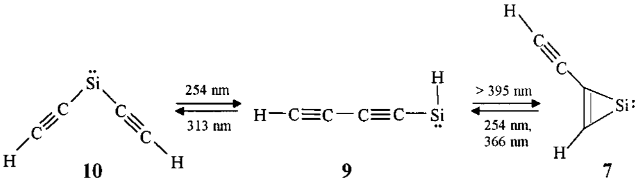
Further support for all these assignments should be reached by generation of the D_2 and $^{13}C_4$ isotopomers of **7**, **9**, and **10** and observing the resulting isotopic shifts in their IR spectra. As suitable precursors disilanes **27** and **29** were selected. Compound **27** was synthesized by the reaction of triflate **15** with deuteroethynylmagnesium chloride[5] and isolated by preparative GC. Synthesis of the required precursor **29** started by reaction of *n*-butylmagnesium chloride and commercially available $^{13}C_2H_2$ yielding ethynylmagnesium [$^{13}C_2$]chloride (**28**). Reaction of this Grignard reagent and triflate **15** led to disilane **29**, which again was isolated by preparative GC.

With both labeled precursors **27** and **29** the same matrix experiments were carried out as with the parent disilane **16**. All observed isotopic shifts corresponded well with the calculated values and, therefore, strongly confirm our assignments (Tables 1 and 2).

Table 2. IR spectral data (BLYP/6-31G*) of butadiynylsilylene (**9**): Experimental (Ar matrix, 10 K) and corresponding calculated and corrected wavenumbers (cm^{-1}). Intensities in parentheses

	mode		$\tilde{\nu}_{calc.}$	$\tilde{\nu}_{corr.}$[a]	$\tilde{\nu}_{obs.}$
a′	CH str		3412.5 (38)	3328.0	3328.0 (w)
		D_2	2629.6 (32)	2564.5	2591.4 (m)
		$^{13}C_4$	3395.6 (38)	3311.5	3313.2 (w)
a′	CC str		2150.7 (16)	2155.7	2155.7 (m)
		D_2	2105.6 (64)	2110.5	2118.2 (vs)
		$^{13}C_4$	2069.2 (14)	2074.0	2074.6 (w)
a′	CC str		2010.6 (17)	2016.4	2016.4 (s)
		D_2	1939.3 (5)	1944.9	1936.3 (vw)
		$^{13}C_4$	1934.1 (18)	1939.6	1941.7 (s)
a′	SiH str		1949.2 (100) [b]	2029.1	2029.1 (vs)
		D_2	1402.4 (100) [c]	1459.9	1474.2 (s)
		$^{13}C_4$	1949.3 (100) [d]	2029.2	2027.1(vs)
a′	CC str		1032.0 (8)	999.6	999.6 (w)
		D_2	1017.3 (19)	985.4	985.1 (w)
		$^{13}C_4$	994.0 (8)	962.8	959.1 (vw)
a′	SiH def		789.3 (31)	ca. 806	ca. 806 (vs)
		D_2	624.4 (29)	ca. 638	ca. 628 (s)
		$^{13}C_4$	785.9 (31)	ca. 803	ca. 803 (vs)
a″	CC def		590.8 (13)	593.7	593.7 (w)
		D_2	466.1 (3)	468.4	–
		$^{13}C_4$	585.1 (0.2)	588.0	527.8 (vw)
a′	SiC str		471.6 (10)	466.0	466.0 (w)
		D_2	455.6 (12)	450.2	456.5 (vw)
		^{13}C	464.0 (10)	458.4	–

[a] $\tilde{\nu}_{corr.} = \tilde{\nu}_{obs.}(C_4H_2Si) / \tilde{\nu}_{calc.}(C_4H_2Si) \cdot \tilde{\nu}_{calc.}$(isotopomer). – [b] Abs. int. 299.6 km/mol. – [c] Abs. int. 157.4 km/mol. – [d] Abs. int. 296.3 km/mol.



$$Me_3Si{-}SiH(OTf)_2 \xrightarrow{2\,DC\equiv CMgCl} Me_3Si{-}SiH(C\equiv CD)_2$$

15 **27**

$$2\,H{-}{}^{13}C\equiv{}^{13}C{-}MgCl + Me_3Si{-}SiH(OTf)_2 \longrightarrow Me_3Si{-}SiH({}^{13}C\equiv{}^{13}CH)_2$$

28 **15** **29**

Conclusion

We were able to generate and matrix-isolate three isomeric silylenes of composition C_4H_2Si, namely diethynylsilylene (**10**), ethynylsilacyclopropenylidene (**7**), and butadiynylsilylene (**9**), by flash pyrolysis of two different precursors and subsequent matrix photolysis of the thermolysis products. The IR spectra of the parent compounds as well as those of the respective C_4D_2Si and $^{13}C_4H_2Si$ isotopomers correspond with the calculated vibrational spectra.

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Experimental Section

Equipment Used for Matrix Isolation, Photolyses, and Pyrolyses: Cryostat for Matrix Isolation: Displex Closed-Cycle Refrigeration System CSA 202 (Air Products). – Light Sources: Low-pressure mercury spiral lamp (Gräntzel, Karlsruhe) with Vycor filter. Mercury high pressure lamp (HBO 200, Osram) and grating monochromator. – Spectrometers: FTIR spectrometer IFS 55 (Bruker), 4000−400 cm^{-1}, all spectra were recorded with 1 cm^{-1} resolution; UV/Vis: Diode array spectrometer HP 8452A (Hewlett-Packard), 190-820 nm, resolution 2 nm.

Pulsed Flash Pyrolyses in Combination with Matrix Isolation: Regulated by a pulsed magnetic valve, a gaseous mixture of the precursor molecule and argon (1:1000) was expanded through a corundum tube (inner diameter 1 mm, length of heated zone 10 mm, heated to ca. 1000°C by a tungsten resistance wire) directly into the high vacuum of the cryostat. Experimental parameters: duration of pulse 0.2 s, equivalent to ca. 1 ml/pulse of gas mixture at 1000 mbar; pulse frequency 10 pulses/min.

General: All reactions were carried out under dry argon or nitrogen. Solvents were dried using standard techniques. All glassware was thoroughly dried in an oven at 130°C prior to use. − NMR spectra were recorded on Bruker AM-400 or AC-200 spectrometers. − IR spectra were recorded on a Bruker IFS 25 spectrometer. − Mass spectra were obtained on a Varian Mat 111 or Varian Mat 311 A spectrometer. − A Carlo-Erba Fractovap 2900 gas chromatograph with a flame ionization detector and a 10 m × 0.3 mm column coated with silicon phase OV 101 was used for analytical gas chromatography. Preparative gas chromatography was performed on a Carlo-Erba Fractovap 2450 using a thermal conductivity detector and helium as the carrier gas (4 m × 6 mm, OV 101). − Trichlorosilane (**17**) and dichlorodiphenylsilane were obtained from Fluka, $^{13}C_2H_2$ (99 atom-% ^{13}C) from Cambridge Isotope Laboratories. Chlorotriphenylsilane was synthesized by reaction of dichlorodiphenylsilane and phenylmagnesium chloride. Triethynylsilane (**18**) was prepared according to a literature procedure[9] by the reaction of three equivalents of sodium acetylide and trichlorosilane in nitrobenzene and purified by preparative GC.

1,1,1-Trimethyl-2,2,2-triphenyldisilane (**12**): Triphenylsilyllithium was generated by stirring of chlorotriphenylsilane with the stoichiometric amount of lithium granules in THF at room temperature for six hours. The resulting solution was added slowly to an excess of chlorotrimethylsilane in THF at 0°C. After aqueous workup disilane **12** was obtained in 82 % yield.

Bromo-2,2,2-trimethyl-1,1-diphenyldisilane (**13**): To 10 g of 1,1,1-trimethyl-2,2,2-triphenyldisilane (**12**), 10 ml of HBr were condensed at −196°C. In order to keep the reaction time as short as possible the reaction flask was taken out of liquid N_2 and immediately put in a water bath of 45°C. After evaporation of the bulk of HBr the formed benzene was removed in vacuo as fast as possible. The crude bromo-2,2,2-trimethyl-1,1-diphenyldisilane (**13**) contained about 15 % of 1,1-dibromo-2,2,2-trimethyl-1-phenyldisilane, as was shown by analytical GC. The crude product was directly used for the next step.

1,1,1-Trimethyl-2,2-diphenyldisilane (**14**): The crude bromodisilane **13** was dissolved in the double volume of diethylether and added dropwise to a suspension of 0.38 g of $LiAlH_4$ (10 mmol) in 25 ml of diethyl ether at 0°C. After stirring overnight aqueous workup with 2 N HCl yielded crude diphenyldisilane **14**. Distillative purification afforded 5.1 g of 1,1,1-trimethyl-2,2-diphenyldisilane (**14**) (65 % referred to **12**) as a colorless liquid of boiling point 110°C/0.1 Torr, which slowly crystallized at room temperature. − IR (neat): ν = 3067 cm^{-1} (CH), 2952 (CH), 2092 (SiH), 1246 ($SiMe_3$). − UV (cyclohexane): λ_{max} (lg ε) = 230 nm (2.36), 261 (2.41). − ^1H NMR (C_6D_6): δ = 0.01 (s, 9 H, $SiMe_3$), 4.94 (s, 1 H, SiH), 6.26 (m, 10 H, aromatic H). − ^{13}C NMR (C_6D_6): δ = −1.36 ($SiMe_3$), 118.89, 129.32, 134.30, 136.03. − ^{29}Si NMR (C_6D_6): δ = −11.22 (SiH), 1.22 ($SiMe_3$). − MS (70 eV); *m/z* (%): 256 (26) [M$^+$], 241 (11), 197 (36), 183 (61), 105 (74), 73 (100). − HRMS calcd. for $C_{15}H_{20}Si_2$ (M$^+$) 256.1104, found 256.1106.

1,1-Diethynyl-2,2,2-trimethyldisilane (**16**): 2,2,2-Trimethyldisilane-1,1-diyl-1,1-bis(triflat) (**15**) was generated by reaction of 1.5 g of 1,1,1-trimethyl-2,2-diphenyldisilane (**14**) (5.8 mmol) with two equivalents of trifluoromethanesulfonic acid (1.7 g) in 20 ml of pentane at 0°C and stirring for 10 min at this temperature. Two equivalents of ethynylmagnesium chloride in THF were added dropwise at 0°C. After completion of the addition all volatiles including the product were removed in vacuo. The solvents were largely removed by distillation. The remaining solution (1 ml) contained about 25 % of 1,1-diethynyl-2,2,2-trimethyldisilane. For the matrix isolation studies it was purified by preparative GC. − IR (neat): ν = 3283 cm^{-1} (CH), 2956 (CH), 2139 (SiH), 2036 (CC), 1249 ($SiMe_3$). − UV (cyclohexane): λ_{max} (lg ε) = 223 nm (3.00). − ^1H NMR (C_6D_6): δ = 0.87 (s, 9 H, $SiMe_3$), 3.15 (d, *J* = 0.2 Hz, 2 H, acetylenic H), 4.77 (m, *J* = 0.2 Hz, 1 H, SiH). − ^{13}C NMR (C_6D_6): δ = −1.54 ($SiMe_3$), 81.24 (*C*≡CH), 98.97 (C≡*C*H) (s). − ^{29}Si NMR (C_6D_6): δ = −79.40 (SiH), −15.80 ($SiMe_3$). − MS (70 eV); *m/z* (%): 152 (5) [M$^+$], 137 (19), 126 (5), 111 (11), 83 (21), 73 (100). − HRMS calcd. for $C_7H_{12}Si_2$ (M$^+$) 152.0478, found 152.0474.

1,1-Diethynyl-3,4-dimethyl-1-silacyclopent-3-ene (**19**): A mixture of 0.60 ml of crude diethynyldisilane **16** and 0.82 g (10 mmol) of 2,3-dimethylbutadiene was passed through an oven at 450°C. The flow pyrolysis was performed in a quartz glass tube (length 33 cm, length of heated zone 25 cm, diameter 15 mm), which was filled with quartz glass Raschig rings. Nitrogen was used as the carrier gas. The yellow pyrolysis product was trapped at 77 K and, after the excess of 2,3-dimethylbutadiene was removed, **19** could be isolated by preparative gas chromatography as a colorless liquid. − IR (neat): ν = 3278 cm^{-1} (CH), 2912 (CH), 2041 (CC). − ^1H NMR (C_6D_6): δ = 1.35 (s, 6 H, CH_3), 1.51 (s, 4 H, CH_2), 1.90 (s, 2 H, CH). − ^{13}C NMR (C_6D_6): δ = 18.77 (CH_3), 25.47 (CH_2), 84.47 (*C*≡CH), 96.00 (C≡*C*H), 127.25 (C=C). − MS (70 eV); *m/z* (%): 160 (100) [M$^+$], 145 (35), 134 (25), 119 (33), 105 (17), 93 (13). − HRMS calcd. for $C_{10}H_{12}Si$ (M$^+$) 160.0708, found 160.0669.

Adducts **20**[10] and **21**[5] were identified by comparison (GC/MS) with authentic probes.

1,1-Bis(deuteroethynyl)-2,2,2-trimethyldisilane (**27**): Deuteroethynylmagnesium chloride was synthesized according to a procedure described earlier[5]. Reaction of this reagent with 0.5 equivalents of triflate **15** in the same manner as in the case of unlabeled **16** (see above) yielded 1,1-bis(deuteroethynyl)-2,2,2-trimethyldisilane (**27**) which also was purified by preparative GC. − IR (gas): ν = 2963 cm^{-1} (CH), 2590 (CD), 2151 (SiH), 1919 (CC), 1254 ($SiMe_3$). − ^1H NMR (C_6D_6): δ = 0.88 (s, 9 H, $SiMe_3$), 4.77 (s, 1 H, SiH). − ^{13}C NMR (C_6D_6): δ = −1.59 ($SiMe_3$), 80.85 (*C*≡CD), 98.65 (C≡*C*D, *J* = 36.2 Hz). − MS (70 eV); *m/z* (%): 157 (6) [M$^+$], 142 (36), 128 (32), 114 (29), 102 (3), 73 (100). − HRMS calcd. for $C_7H_{10}D_2Si_2$ (M$^+$) 154.0603, found 154.0586.

1,1-Diethynyl-2,2,2-trimethyldisilane-$^{13}C_4$ (**29**): About 200 ml of gaseous $^{13}C_2H_2$ were frozen out at −196°C. At this temperature, a solution of 18 mmol *n*-butylmagnesium chloride in THF was added dropwise. By slow warming up to 0°C and stirring as soon as possible, a maximum conversion of the acetylene could be achieved. The reaction of this Grignard compound with triflate **15** was carried out as described above and yielded after separation by preparative GC 45 µl of disilane **29** as a colorless liquid. − IR (gas): ν = 3321 cm^{-1} (CH), 2066 (CC), 2058 (SiH). − ^1H NMR (C_6D_6): δ = 1.05 (s, 9 H, $SiMe_3$), 3.33 (d×d×m, ^1J = 173.8 Hz, ^2J = 147.3 Hz, 2 H, acetylenic H), 4.94 (m, 1 H, SiH). − ^{13}C NMR (C_6D_6): δ = −1.54 ($SiMe_3$), 81.45 (d, *J* = 173.8 Hz, *C*≡CH), 99.09 (d, *J* = 147.3 Hz, C≡*C*H). − MS (70 eV); *m/z* (%): 156 (10) [M$^+$], 141

(37), 113 (21), 85 (39), 73 (100). − HRMS calcd. for $^{12}\mathrm{C2}^{13}\mathrm{C4H9Si2}$ ($M^+ - CH_3$) 141.0377, found 141.0295.

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